

# Decoherent Histories and Non-adiabatic Quantum Molecular Dynamics Simulations.

Eric R. Bittner

*Department of Chemistry, University of Houston,  
Houston TX 77204*

Peter J. Rossky

*Department of Chemistry and Biochemistry, University of Texas at Austin,  
Austin, TX 78712*

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The role of quantum coherence loss in mixed quantum-classical dynamical systems is explored in the context of the theory of quantum decoherence introduced recently by Bittner and Rossky. (J. Chem. Phys. **103**, 8130 (1995)). This theory, which is based upon the consistent histories interpretation of quantum mechanics, introduces decoherence in the quantum subsystem by carefully considering the relevant time and length scales over which one must consider the effects of phase interference between alternative histories of the classical subsystem. Such alternative histories are an integral part of any quantum-classical computational scheme which employ transitions between discrete quantum states; consequently, the coherences between alternative histories have a profound effect on the transition probability between quantum states. In this paper, we review the Bittner-Rossky theory and detail a computational algorithm suitable for large-scale quantum molecular dynamics simulations which implements this theory. Application of the algorithm towards the relaxation of a photoexcited aqueous electron compare well to previous estimates of the excited state survival time as well as to the experimental measurements.

## I. INTRODUCTION

A key issue which has emerged in describing electronic transitions in the condensed phase is the proper treatment of the short-lived phase coherence of the electronic and nuclear (bath) wavefunction. The essence of the effect becomes clear if one considers the behavior of an electronic quantum system in a classical bath. In such a mixed quantum-classical system, the classical dynamics of the bath nuclei follow along a given adiabatic potential surface associated with one of the eigenstates of the electronic Hamiltonian. Thus the potential felt by the nuclear degrees of freedom will depend strongly upon the quantum state of the electronic degrees of freedom. The fundamental distinction between quantum mechanics and classical mechanics is that a quantum system can evolve into a coherent linear superposition of states. This leads to a rather profound ambiguity in describing the forces between the quantum and classical subsystems. Furthermore, quantum mechanics forces us to consider the effect of all alternative histories or pathways, including those of the classical bath, when computing quantum transition probabilities. Thus, as the electronic wavefunction evolves from an initially pure eigenstate to a coherent superposition of eigenstates, various alternative pathways for the bath particles begin to emerge, each associated with dynamics starting from an initial nuclear configuration and electronic state and ending in a different final nuclear configuration and final electronic eigenstate. As the nuclear dynamics for the different quantum (electronic) states diverge, phase coherence between the alternative histories is lost due to the increasing differences between the classical actions associated with each alternative nuclear path. This effect is known as quantum decoherence.<sup>1</sup>

Because quantum decoherence acts to suppress the formation of superposition states, it diminishes profoundly the transition probability between quantum states coupled by the nuclear dynamics. When the loss of quantum phase coherence between the electronic states is neglected and no longer enters directly into the computation of making an electronic transition, which is a typical approximation made in mixed quantum-classical treatments, one can show that the result will be an incorrect estimation of the transition probabilities

and other associated physical observables.<sup>2</sup> Because of the tremendous utility of mixed-quantum classical treatments in simulating condensed phase phenomena, it is of tantamount importance to be able to properly incorporate the effects of quantum decoherence into these simulations.

Recently, we have presented a theory of quantum decoherence which is suitable for condensed phase quantum molecular dynamics simulations.<sup>2</sup> This approach is based upon an interpretation of quantum mechanics introduced by Griffiths<sup>3</sup>, Omnès<sup>4,5</sup>, and Gell-Mann and Hartle<sup>6-8</sup> over roughly the past 10 years. This interpretation of quantum mechanics, termed “consistent” or “decoherent” histories, has generated a great deal of attention in the field of quantum cosmology.<sup>9-11</sup> We have also applied and extended the formalism to study coherence effects in physically realistic condensed phase problems<sup>12,13</sup>. This work has lead to a number of advances in designing computational algorithms which incorporate a consistent description of quantum decoherence and to a deeper understanding of the role that quantum decoherence plays in condensed phase chemical processes and molecular level descriptions of the decoherence process.<sup>2,12-14</sup> These theoretical advances have also offered a tangible solution to a specific long standing puzzle regarding the solvent isotope effect on the non-radiative lifetime of an excess electron in H<sub>2</sub>O and D<sub>2</sub>O and offer a plausible explanation of the lack of an observed solvent isotope effect.<sup>15-18</sup>

In this paper, we give the details of our computational algorithm based upon consistent quantum histories and its application in a full scale quantum molecular dynamics simulation of the relaxation of an excited excess electron in H<sub>2</sub>O. The simulations presented in this paper represent the first application of the Bittner-Rosky decoherence theory in a full scale simulation of a condensed phase system. The aqueous electron provides perhaps the simplest example of electronic dynamics in the condensed phase. At the same time, aqueous electrons are of particular importance since they play a prominent role in the broad area of radiation chemistry of water. In spite of intensive experimental and theoretical study since identification of the hydrated electron over 30 years ago, many dynamical features of electron solvation have remained incompletely understood, largely due to the extremely fast

time scales on which electronic relaxation occurs.<sup>15</sup> Newly developed femtosecond spectroscopic techniques are now providing glimpses of the details of condensed phase electronic dynamics. From a theoretical standpoint, the aqueous electron is an ideal test case for new condensed phase theories. Recent theoretical advances in treating condensed phase electronic dynamics<sup>19–23</sup> has led to an exceptional interplay between theory and experiment, helping to unravel many subtle dynamical aspects of this system.

The remainder of this paper proceeds as follows: In the next section we review the consistent histories methodology as it applies toward developing a computational algorithm for condensed phase simulations. We then give the results of quantum MD simulations of the non-adiabatic relaxation dynamics of an excited excess aqueous electron which employ the consistent histories algorithm and compare the present results to previous estimates of the non-adiabatic electronic transition rate by Schwartz, Bittner, Prezhdo, and Rossky (SBPR)<sup>12</sup>, to earlier results presented by Schwartz and Rossky which employed a constant 1 fs coherence time scale throughout,<sup>22–24</sup> as well as to the experimental data of Kimura *et al.*<sup>16–18</sup> Finally, we comment upon the utility of the present algorithm and discuss its limitations as well as future extensions and improvements.

## II. THEORETICAL METHODS

### A. Coherence Between Switching Paths

Let us consider the evolution of an initial quantum state  $|i(R_o)\rangle$ , taken as an adiabatic eigenstate of the quantum mechanical Hamiltonian for initial bath (or classical) configuration  $R_o$ , along a switching path,  $R^\alpha(t)$  which begins at  $R_o$ . Along the course of this path, we determine at various time intervals whether or not a quantum transition has occurred according to a stochastic switching criteria and modifying the classical dynamics accordingly. The fundamental notion of having classical particles switch between discrete quantum states was originally pioneered by Tully<sup>26</sup> in the early 1970's. Subsequently, various computa-

tional schemes have been developed which incorporate quantum switching into the classical dynamics and improve upon Tully's original idea. Most notably are the stationary phase surface hopping algorithms developed by Webster, Friesner, and Rossky<sup>20,21</sup> and further by Coker and co-workers<sup>25,31,33,34</sup>, as well as the Molecular Dynamics with Quantum Transitions algorithm of Tully and co-workers<sup>28,30</sup>. The classical switching path contains a record of the outcome of each switching attempt and can thus be written as a time ordered sequence of events,

$$R^\alpha(t) = \{R_o^{\alpha_o}, \dots, R_j^{\alpha_j} \dots, R_n^{\alpha_n}\}. \quad (1)$$

The superscript  $\alpha_j$  denotes the switching outcome at time-step  $j$  and  $\alpha_o = i$  corresponding to our choice of the initial quantum state. Two such paths are shown schematically in Fig. 1 where we plot the eigenenergy of the occupied state along the path as a function of time. Changes in the quantum state imply that there is a corresponding sudden change in the forces exerted on the classical particles over the course of its evolution. The result is that different sequences of switching events will lead to rapidly diverging paths.

Along a given switching path,  $R^\alpha(t)$ , the partial transition amplitude between an initial and final quantum state,  $|i(R_o)\rangle$  and  $|f(R_f)\rangle$  respectively, is given by

$$\begin{aligned} T_{if}[R^\alpha(t)] &= \langle f(R_f^\alpha) | e^{-i \int_{t_o}^{t_f} ds H_Q[R^\alpha(s)]} | i(R_o) \rangle e^{+iS[R^\alpha(t)]} \\ &= U_{if}[R^\alpha(t)] e^{+iS[R^\alpha(t)]}, \end{aligned} \quad (2)$$

where  $U_{if}[R^\alpha(t)]$  is the transition amplitude for the quantum subsystem (with Hamiltonian  $H_Q$ ) and  $S[R^\alpha(t)]$  is the classical action computed along the switching path  $R^\alpha(t)$ , i.e.

$$S[R(t)] = \int_{t_o}^{t_f} dt \left\{ \frac{m}{2} \dot{R}(t)^2 - V_C(R(t)) \right\}. \quad (3)$$

Here,  $V_C$  is the interaction potential coupling the classical particles. The probability of starting in some initial state  $|i(t_o)\rangle$  ending up in a given final quantum state,  $|f(t_f)\rangle$ , at some time  $t_f$  is computed by summing over all possible switching paths which connect the initial and final quantum states. Averaging over initial configurations, the reduced transition probability for a mixed quantum-classical system is

$$\begin{aligned}
P_{if}(t_f) &= \left\langle \sum_{\{R^\alpha(t), R^\beta(t)\}} T_{if}[R^\alpha(t)] T_{if}^\dagger[R^\beta(t)] \rho_i(R_o) \right\rangle_o, \\
&= \left\langle \sum_{\{R^\alpha(t), R^\beta(t)\}} U_{if}[R^\alpha(t)] \rho_i(R_o) U_{if}^\dagger[R^\beta(t)] e^{i(S[R^\alpha] - S[R^\beta])} \right\rangle_o,
\end{aligned} \tag{4}$$

where  $\rho_i(R_o)$  is the probability density of being in the initial state, the average,  $\langle \cdots \rangle_o$ , is taken over initial configurations, and the sum is over pairs of switching paths

$$\{R^\alpha(t), R^\beta(t) | R^\alpha(0) = R_o, R^\beta(0) = R_o\} \tag{5}$$

which start at the initial configuration,  $R_o$ , with the quantum state in the initial state and end at any final configuration with the quantum state in state  $|f\rangle$  at  $t_f$ .

According to this last equation, the transition probability for the quantum subsystem is dependent upon interferences between the various alternative pairs of switching pathways. Thus, in order to correctly compute the populations of the electronic states at some later time, one must perform a sum over all alternative paths that the bath can take. In a practical sense, this amounts to launching a swarm of trajectories from each initial starting point and computing the switching probabilities (i.e. branching ratios for the swarm) using Eq. 4. However, this approach has the distinct disadvantage that one must initialize a large enough swarm of trajectories in order to effectively sample the distribution of switching paths originating from each initial configuration. So, while formally correct and tractable in small dimensional systems, the tremendous computational overhead required to implement Eq. 4 directly for a large number of classical variables is prohibitive.

Next, we present an alternative derivation of the quantum survival and transition probabilities which uses only a single switching path explicitly. The formalism is motivated by the observation that at short times, there will be a significant contribution from the phase interferences between two alternative paths with similar histories, necessitating a coherent sum over paths, while at longer times the action difference between two paths will become very large and phase interference effects from alternative paths will become negligible. The time scale separating these two regimes is the quantum coherence time scale.

## B. Consistent Histories

Let us define the space of paths,  $\mathcal{Z}$ , as consisting of all continuous paths connecting some initial system/bath state  $R_0^\alpha$  to the final state  $R_f^\beta$  labeled by a set of quantum numbers,  $\{\alpha_j\}$  and a classical bath variable,  $R$ . Define also a set of subspaces of  $\mathcal{Z}$  labeled by  $\Delta(R^\alpha)$  which are the spaces of paths taken by the quantum subsystem which are parameterized by the paths taken by the bath. The full space of paths is the continuous union of all the various subspaces.

$$\mathcal{Z} = \biguplus_{\alpha} \Delta(R^\alpha) \quad (6)$$

These paths are *completely fine grained histories* since the values of the each paths can be specified at all times and one can compute the partial amplitude along any one of the paths in  $\mathcal{Z}$ . Furthermore, by integrating over the individual “quantum” subspaces one obtains Eq. 2,

$$\begin{aligned} T_{\alpha\beta}[R^\alpha] &= \int_{\Delta(R^\alpha)} Dx \exp(i(S_Q[x, R^\alpha] + S[R^\alpha])) \\ &= U_{if}[R^\alpha(t)]e^{+iS[R^\alpha(t)]}. \end{aligned} \quad (7)$$

A fundamental property of quantum mechanics is that fine grained histories can not be assigned probabilities, only amplitudes. In order to make predictions based upon the theory of probabilities, *coarse graining* of histories must be introduced. Coarse graining is accomplished when a “reduced” history is constructed by summing over sets of fine grained histories at a particular time. Coarse grained histories can be assigned probabilities, that is, integrating over coarse grained histories is equivalent to integrating over probabilities.

Coarse graining of histories arises naturally whenever we try to mix quantum with classical dynamics. As different classical switching paths emerge from a common origin, the space of quantum paths parameterized by one switching path will diverge from the space of quantum paths parameterized by another. As the “overlap” between subspaces decays (corresponding to different classical dynamics), the originally fine grained space of paths,  $\mathcal{Z}$ ,

becomes coarse grained into separate subspaces,  $\{\Delta(R^\alpha)\}$  as time goes on. Consequently, transition probabilities are computed by first integrating coherently over the fine grained sets of paths to get the transition amplitude say along one classical switching path, then summing incoherently (i.e. adding as ordinary probabilities) over coarse grained sets.

Quantum decoherence effects can be consistently incorporated into mixed quantum-classical systems by recognizing that restricting the quantum evolution to given classical pathways is equivalent to making a series of quantum measurements on the total system. Furthermore, the quantum coherence time is the time scale which characterizes how often such “measurements” occur<sup>2</sup>. The classical path sequence shown in Fig. 1 is an example of a quantum mechanical history. Along this history, the time evolution operator for the quantum system can be written equivalently as a time ordered sequence of alternating quantum projection operators and unitary evolution operators

$$\hat{C}[R^\alpha(t)] = \hat{U}_n \hat{P}^{\alpha_{n-1}} \dots \hat{U}_1 P^{\alpha_1} \hat{U}_0 \quad (8)$$

where the projections at each time interval are members of complete sets representing the total set of possible outcomes,

$$\sum_{\alpha_i} \hat{P}^{\alpha_i} = 1, \quad (9)$$

and

$$\hat{U}_n = e^{-i \int_{t_{n-1}}^{t_n} ds H[R^\alpha(s)]} \quad (10)$$

is the unitary evolution operator for the quantum wavefunction along a segment of the switching path.

The decoherence time scale sets a characteristic time interval between subsequent applications of the projection operators. This time scale is roughly the time scale for alternative stationary trajectories of the nuclear bath to diverge sufficiently such that the difference in action between the two paths in Eq. 4 is large. In Ref.12 we suggested that coherence time scale is related to the time scale for the decay of the overlap integral between nuclear wavefunctions evolving on different adiabatic potential energy surfaces. During the coherence



interval, transition amplitudes are added coherently according to the rules of quantum mechanics. Application of the projection operators destroys the coherences and one is left with transition probabilities which are then added according to the rules of standard probability theory. Within this approach, Eq. 4 is equivalent to

$$\begin{aligned} P_{i \rightarrow f}(t) &= \left\langle \sum_{\{R^\alpha(t)\}} \langle f_n | \hat{C}[R^\alpha(t)] \rho_i(R_o) \hat{C}^\dagger[R^\alpha(t)] | f_n \rangle \right\rangle_o \\ &= \left\langle \sum_{\{R^\alpha(t)\}} \langle f_n | \hat{U}_n \hat{P}^{\alpha_{n-1}} \dots \hat{P}^{\alpha_1} \hat{U}_1 \rho_i \hat{U}_1^\dagger \hat{P}^{\alpha_1} \dots \hat{P}^{\alpha_{n-1}} \hat{U}_n^\dagger | f_n \rangle \right\rangle_o, \end{aligned} \quad (11)$$

where  $|f_n\rangle = |f(R^{\alpha_n})\rangle$  is the final quantum state at the end of path  $R^\alpha(t)$ .

When the time intervals  $\delta t_n = t_n - t_{n-1}$  are members of a Poisson distribution, the probability of maintaining coherence over a given interval,  $t$ , follows from the exponential deviate

$$\pi(t) = \int_0^t ds \frac{e^{-s/\tau}}{\tau} = 1 - e^{-t/\tau}, \quad (12)$$

and  $\tau$  is the characteristic decoherence timescale. Thus, over a short time interval,  $\delta t$ , where the probability of collapsing the wavefunction is

$$\pi(t) = \delta t / \tau + \mathcal{O}(\delta t^2), \quad (13)$$

the reduced density matrix of the quantum system evolves as

$$\rho(t + \delta t) = (1 - \delta t / \tau)(\rho(t) + i\delta t[H, \rho]) + \delta t / \tau \mathcal{R}[\rho]. \quad (14)$$

where  $\mathcal{R}[\rho]$  is a “reduction mapping” of the density matrix  $\rho$  which projects out the diagonal elements of the quantum density matrix (the populations) killing off the coherences between the quantum states.

Taking the limit of  $\delta t \rightarrow 0$  in Eq. 14 and identifying  $\tau$  as the decoherence timescale  $\tau_D$  we arrive at the master equation for the quantum density matrix.

$$\begin{aligned} \dot{\rho}(R) &= i[H(R), \rho(R)] - \frac{1}{\tau_D}(\rho - \mathcal{R}[\rho(R)]), \\ &= \mathcal{L}(R)\rho - \frac{1}{\tau_D}(\rho(R) - \mathcal{R}[\rho(R)]). \end{aligned} \quad (15)$$

The first term in this equation contains the Liouvillian of the quantum system,  $\mathcal{L}(R) = i[H(R), \cdot]$ . Evolution of the quantum system under this term alone is unitary and non-dissipative. The second term introduces *quantum decoherence* into the dynamics of the quantum subsystem. The coherences originally in the quantum subsystem decay due to the series of measurements imposed by the environment. Although energy exchange does not appear explicitly in Eq. 15, energy exchange between the system and the bath is explicitly included through dynamics of the bath variable  $R(t)$  treated separately.

In other theories of quantum relaxation, such as the spin-boson model<sup>35,36</sup>, the Redfield equations<sup>37–41</sup>, or Liouville space methods<sup>42</sup>, both decoherence and dissipation are treated implicitly through effective equations of motion for the bath, thus losing the molecular level information about the underlying dynamics of the bath. In our treatment, dissipation is included *explicitly* through the classical molecular dynamics of the condensed phase medium, thus we are able to retain a molecular level description of the bath while quantum decoherence is treated implicitly in order to avoid summing over alternative pairs of classical paths.

It is important to note that the form of the projections and the coherence time scale (and the resulting master equation) are directly related to the forces coupling the quantum system to the bath and hence are very dependent upon the choice of basis used to represent the quantum subsystem. In the present application of our theory, we assume that the projections periodically resolve the quantum subsystem into the adiabatic states with a time scale determined by the average decay time of the Franck-Condon overlap between nuclear wavefunctions initialized on the different adiabatic surfaces at the instantaneous nuclear coordinates.<sup>12</sup> A more detailed analysis of this assumption is forthcoming.<sup>14</sup>

Perhaps the most important physical consequence of decoherence for chemical physical applications is the overall reduction of the transition probabilities between different quantum states. In order for a quantum system to make a transition from one state to another, the system must form a coherent superposition between the states. The ease with which these coherences form reflects the strength of the coupling between the two states. Decoherence,

on the other hand, reflects the strength of the system-bath coupling. When a quantum system evolves into a superposition state, the destructive interferences between divergent alternative switching paths leading to the final state destroys the coherence in the quantum subsystem, hence, reducing the likelihood of making a transition into the final state.<sup>2</sup>

### III. SIMULATIONS

The simulation techniques employed here are nearly identical to those used in earlier work by Murphrey and Rossky studying both the relaxation of electrons photo-injected into neat water<sup>20,29</sup> as well as the present case of photoexcitation of equilibrium hydrated electrons by Schwartz and Rossky. The exceptions regard the treatment of the quantum coherences detailed below.<sup>23,24,43</sup> Briefly, the model consists of 200 classical SPC water molecules with the addition of internal flexibility<sup>44</sup> and one quantum electron in a cubic cell of side 18.17 Å (corresponding to a solvent density of 0.997 g/ml) with standard periodic boundary conditions at room temperature. The electron-water interactions were described with a pseudo-potential,<sup>45</sup> and the equations of motion integrated using the Verlet algorithm with a dynamical time step of 1 fs in the microcanonical ensemble.<sup>46</sup> The adiabatic eigenstates at each time step were computed via an efficient iterative and block Lanczos scheme utilizing a  $16^3$  plane wave basis<sup>20</sup> The lowest 6 eigenstates were used as a basis for propagating the quantum wavefunction and to compute the stationary phase paths for the nuclear dynamics. Explicit details of these methods are discussed elsewhere.<sup>20</sup>

#### A. Consistent Histories Algorithm

Quantum decoherence was incorporated into the simulation through the Consistent Histories theory discussed above. The computational algorithm given below follows directly from Eq. 11 and the coherence time intervals were chosen from a Poisson distribution with characteristic time scale  $\tau_D = 3.1$  fs which was derived from our previous estimates of the coherence time scale for an electron in H<sub>2</sub>O when the excited state is nearly solvated. As

discussed in a previous paper, this time scale was estimated by computing the average decay time of the overlap of frozen Gaussian vibrational wavefunctions evolving on different adiabatic potential energy surfaces by sampling a large number of nearly equivalent excited state configurations. This is in marked contrast to previous simulations on this system in which coherences between electronic states were not maintained beyond 1 fs. The consistent histories algorithm proceeds as follows:

1. Determine new coherence interval from Poisson distribution of possible intervals with characteristic time scale  $\tau_D$ .
2. Propagate the quantum wavefunction over this time scale while self consistently evolving the classical degrees of freedom. At the end of each dynamical time step  $h \leq \tau_D$ , determine the switching path followed by the classical variables using the stationary phase algorithm developed by Webster, *et al.*<sup>20,21</sup> modified such that coherence in the quantum wavefunction is maintained over the entire coherence interval. We also note that the stationary phase switching path is determined in a piece-wise continuous fashion by selecting intermediate quantum states every dynamical time step. This is to avoid the computational overhead of computing variationally the stationary phase trajectory over relatively long time intervals. So long as  $\tau_D$  is no longer than a few dynamical time steps, this approximation should not be too extreme; however, certain pathological cases can be invented in which this approximation does break down.
3. If either a switch occurs in the time interval or we reach the end of the interval, the quantum wavefunction is collapsed using the projection operators discussed above.
4. Repeat.

## B. Results

In Fig. 2 we plot the switching times from the excited state to the ground state for a total of 23 simulation runs. The starting configurations were generated by performing

a 35 ps simulation in which the electron was prepared in the ground state and 16 initial configurations were chosen whenever the energy difference between the ground state and one of the p-like excited states become resonant with the excitation laser (1.7 eV).<sup>16–18</sup> These starting configurations were identical to configurations used previously by Schwartz and Rossky in their work on this system.<sup>23,24,43</sup> Following the initial excitation, the system was allowed to evolve. During this time, the energy gap between the p-states and the s-state narrowed to  $\approx 0.5\text{eV}$  as the excited state was solvated by the surrounding water molecules. The simulation continued until a switch from the excited state to the ground state was recorded. Immediately after the switch, the energy gap between the occupied ground state and the first excited state widened dramatically as the solvent responded to the new electronic state. The average and median switching times from these simulations are compiled in Table 1.

In order to test the sensitivity of the switching times to the choice of sequence of coherence intervals, five configurations were “recycled” by using different random number sequences for the coherence time intervals to generate different switching paths starting from the same initial configuration. For each such pairs of paths, the classical dynamics were identical up until the earlier switching time when one of the paths switched from the excited state to the ground state. However, since the coherences between the different quantum states were killed off at randomly different times for each path, each path sampled a different probability distribution function for making a switch at each MD time step. Hence any correlations between switching times resulting using the same initial configuration reflect correlations in the distribution of coherence time intervals. Given that there is typically a 100 fs time difference between pairs of data (in one case a 530 fs difference) which is roughly 1/3 of the average survival time scale of the excited state, we find very little correlation between the switching times originating from the same initial configuration.

The excited state survival probability reflects not only the probability of making a transition from the excited state to the ground state, it also reflects the solvation dynamics of the non-equilibrium excited state following its preparation. Initially, the energy gap between

the excited and ground state is very wide and a non-adiabatic transition between the states is highly unlikely. However at later times, after the excited state has begun to be solvated by the surrounding water molecules, the energy gap closes considerably and nonadiabatic transitions become more likely. The solvation dynamics of this system have been extensively studied previously by Schwartz and Rossky.<sup>23,24,43</sup> Their results for the solvation response, defined as the normalized autocorrelation of the energy gap between the ground and excited states, indicates a rapid 24 fs initial Gaussian component which makes up roughly 40% of the response followed by a longer time 240 fs exponential decay which makes up most of the remainder.

As the excited state is solvated by the surrounding water molecules, the energy gap between the excited state and the ground state narrows to its equilibrium value. Furthermore, from first order perturbation theory, we expect that the electronic transition rate to be inversely proportional to the magnitude of the energy difference between initial and final states. Thus, a simple model for the excited state survival probability can be written

$$\frac{\partial P(t)}{\partial t} = -\frac{k_{\text{eq}}}{\tilde{\omega}(t)} P(t) \quad (16)$$

subject to the initial condition  $P(0) = 1$ . Here,  $k_{\text{eq}}$  is the non-adiabatic transition rate for the solvated excited state and  $\tilde{\omega}(t)$  is the average energy gap normalized to the average energy gap of the solvated excited state.  $\tilde{U}(t)$  is also related to the solvation response  $S(t)$  by

$$\tilde{\omega}(t) = \frac{\langle\omega_o\rangle S(t) + \langle\omega_{\text{eq}}\rangle(1 - S(t))}{\langle\omega_{\text{eq}}\rangle}. \quad (17)$$

The solvation response can be modeled as short time Gaussian decay followed by a longer time exponential relaxation,<sup>22-24,47</sup>

$$S(t) = Ae^{-1/2(t/t_G)^2} + (1 - A)e^{-t/t_E}. \quad (18)$$

In Fig. 3, we plot  $\tilde{\omega}(t)$  using a parameteric fit to the solvation response function obtained from our simulations:  $A = 0.38$ ,  $t_G = 0.38$  fs,  $t_E = 240$ fs. These parameters agree exactly

with those obtained by Schwartz and Rossky<sup>22–24</sup> for this system. This comes as no surprise since our inclusion of quantum coherence effects does not effect the computation of the interaction forces between the excited electron and the water molecules. At short times, when  $\tilde{U}(t) > 1$ , the nonadiabatic transition rate will be small since the energy gap is large. At long times  $\tilde{\omega}(t) \rightarrow 1$  as the energy gap relaxes to its equilibrium value. Thus,  $k_{eq}$  is the exponential decay constant of the excited state population once the excited state is fully solvated.

The solution of Eq. 16 is the one parameter family of curves given by

$$P(t) = \exp \left( -k_{eq} \int_0^t \frac{ds}{\tilde{\omega}(s)} \right) P(0). \quad (19)$$

Using a non-linear fitting procedure, we fit our data to this model to obtain an estimate of the equilibrium nonadiabatic lifetime of 241 fs with a  $\chi^2 = 1.707$ . A plot of our data superimposed on this fit is given in Fig. 2. Interestingly enough, our data does not fit this simple model as nicely as the data given by Schwartz and Rossky.<sup>22–24,47</sup> This suggests that the longer coherence times used in this study imparts a non-trivial memory dependency into the survival probability which is inadequately captured in Eq. 16.

As expected, the lifetimes reported here (Table 1) are consistently shorter than the lifetimes reported by Schwartz and Rossky<sup>22–24,47</sup> in which a constant 1 fs coherence time scale throughout their simulations, thus emphasizing the profound sensitivity of these simulations to the coherence time scale. Furthermore, our results are consistent with the estimated lifetimes reported in SBPR<sup>12</sup> where the effective equilibrium lifetime was estimated as a function of coherence time by reanalyzing the transition amplitudes computed in the original Schwartz and Rossky simulations with the coherence time scale estimated from a frozen Gaussian approximation to the nuclear wavefunction.

#### IV. DISCUSSION

In this paper we have briefly described the results of our work towards a molecular level description of quantum relaxation phenomena. Here we have focused exclusively upon the

role that transient quantum mechanical coherences between the solvent and the solute play in the electronic relaxation of an excited solute species. In mixed quantum-classical computer simulations, fundamental assumptions about the decay of these coherences produce direct manifestations on the computed quantum mechanical transition rates and must be included consistently in order to make realistic predictions and comparisons.<sup>2,12</sup>

The computational algorithm, based upon the so-called consistent histories interpretation of quantum mechanics, provides both the molecular level underpinnings of quantum decoherence and the computational means for properly including decoherence effects in non-adiabatic quantum-molecular dynamics simulations. According to the rules of ordinary quantum mechanics, a quantum system will evolve into a coherent superposition of alternative states. In our decoherence theory, this coherence is dissipated due to the differences in the forces exerted on the bath by alternative states involved in the superposition. Thus, on short scales, a quantum system in a bath will obey the rules of ordinary quantum mechanics and evolve into a coherent superposition of states, whereas on longer time scales, the coherences between states are diminished and the quantum system must be described as statistical (i.e. incoherent) mixture of states. As the quantum system interacts continuously with the bath, coherences between states are continuously created by non-adiabatic coupling and damped by the divergence in the bath dynamics induced by the system-bath coupling.

This subtle interplay between coupling and decoherence and the subsequent dependency of transition rates on the decoherence time scale has profound implications for a variety of condensed phase chemical dynamics including: internal conversion and internal vibrational energy redistribution (in which the bath is comprised of all the modes of the molecules except for the one mode of interest), electronic energy transfer between molecules or different parts of the same molecule, and charge transfer reactions including proton and electron transfer. In these latter examples, both the condensed phase environment and the internal motions of the molecules act as a bath which couples the quantum states together. The decay of quantum coherence, which depends upon the frequencies and populations of the bath modes coupled to the quantum system will determine the extent to which the non-adiabatic



coupling can act to allow the chemical reaction to proceed. Changes in the spectral density due to isotopic changes in the bath can have a substantial impact on non-adiabatic chemical dynamics.<sup>12</sup> Furthermore, the decay of quantum coherence can determine the adiabaticity for a chemical reaction.

Perhaps the two major lacunae in our present theory is the explicit dependency upon an *a priori* estimate of the coherence time scale and the fact that this time scale remains fixed throughout the calculation. As mentioned above, we estimated this time scale by computing the average decay time of the overlap of a product of Gaussian coherent states evolving on different adiabatic potential energy surfaces. In this estimate, the individual widths of the coherent state wavefunctions centered about the initial phase space points of the classical nuclei are set to be proportional to the thermal DeBroglie wavelength of each nuclei. Although physically realistic for a variety of situations, this does leave the coherence *length scale* (i.e. the widths) as an adjustable parameter. While the effects of changing the coherence length scale over a broad range have not been systematically studied, results from our previous work demonstrate that the non-adiabatic transition is quite sensitive to changes in the coherence time scale and hence will be sensitive to changes in the coherence length scales. Furthermore, as the bath explores various regions of the quantum potential energy surface, the force differences which give rise to the decay of the quantum coherences<sup>12</sup> should vary from one configuration to the next. Current progress is underway towards obtaining both the coherence length and time scale during the course of the non-adiabatic simulation *ab initio* by examining the quantum mechanical fluctuations of the bath particles about their stationary phase paths.

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## Tables

TABLE I. Excited state lifetimes for the aqueous electron. (SR= Schwartz and Rossky, J. Chem. Phys. **101** 6902 (1994). SBPR = Schwartz, Bittner, Prezhdo, and Rossky, J. Chem. Phys. **104** 4942 (1996)). The coherence times used in each study are listed in parentheses.

	Present (3.1 fs )	SR (1 fs)	SBPR (2.8-3.1 fs) <sup>(a)</sup>
Median	338 fs	630	—
Average	384	730	—
Equilibrium	234	450	310-270

(a.) Only Equilibrium lifetimes considered.

## Figure Captions

FIG. 1. Energy eigenvalues and quantum populations along different switching paths for the electron in water. Shown in the upper graph are the energy eigenvalues of the occupied electronic state for two possible switching paths with the occupations shown in the lower plot. Following promotion to the excited state, the electron makes a series of stochastic hopping attempts between the initial and final states with two possible outcomes shown.

FIG. 2. Excited state cumulative survival probability as a function of time following initial excitation. Superimposed points (A) are the switching times from the simulations. Curve B is the fit of the data to the energy gap relaxation model given by Eq. 22 and curve C is a fit of the data to a Gaussian. See text for details.

FIG. 3. Plot of the normalized energy gap,  $\omega$ , between the ground and occupied excited state following initial excitation.







